UNPUBLISHED PRELIMINARY DATA

THE BINARY EUTECTIC AS A THERMAL ENERGY STORAGE SYSTEM: EQUILIBRIUM PROPERTIES*

[redacted]

22p

By

G. R. Belton+ and Y. Krishna Rao++ [1963] 29 refs

Pennsylvania U., Philadelphia Towne School of Civil and Mechanical Engineering

Presented at 6th Natl. ASME-AIChE Heat Transfer Conf., Boston, Aug

N64 33777	1
(ACCESSION NUMBER)	(THRU)
22	1
(PAGES)	(CODE)
CR-51748	13
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

FACILITY FORM 602

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ABSTRACT

The method is reviewed for the calculation of heats of fusion of binary eutectic systems of metals or salts from the available thermodynamic data. A preliminary survey has been made to find metals, metallic compounds and binary systems of these substances which could serve as constant temperature heat reservoirs for thermal energy storage. AUTHOR

OTS PRICE

XEROX $ 4.00 FS

MICROFILM $ 1.50 MF

*This paper is to be presented at 6th National Heat Transfer Conference, Boston, Massachusetts, not to be published in the permanent literature in this form.

This work was supported by the National Aeronautics and Space Administration under contract NsG-316 to the Institute for Direct Energy Conversion of the Towne School of Civil and Mechanical Engineering of the University of Pennsylvania.

+Assistant Professor, Department of Metallurgical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania

++Research Fellow, Department of Metallurgical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania

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INTRODUCTION

A solar powered heat engine or thermionic energy converter in orbiting space vehicles require some means of energy storage for power while they are in shade. Batteries have been used to store the energy in electric form. The energy losses and high system weight associated with the use of batteries make it desirable to look for alternative means of energy storage. Metals and metallic salts could serve as excellent reservoirs for thermal energy storage. The amount of energy that can be stored isothermally is limited by the heat of fusion of the substance considered. The melting point of the metal or metallic salt under consideration would determine the upper cycle temperature. The binary eutectics of light weight metals and compounds offer a means of obtaining a wide choice of operating temperatures without significantly lowering the available heat.

As an example, the melting point and the heat of fusion of lithium hydride are $959.6^{\circ}K$ and 7.0 ± 2.0 k.cal./mol.[6] respectively. So the available heat would be 880 ± 250 cals./gm. which is the highest for any compound. However, it is very difficult to find a suitable refractory material which will contain molten lithium hydride and which is impermeable to the hydrogen produced by dissociation of the hydride. Therefore, compounds and metallic systems which can be contained without much difficulty are sought and a few of them are presented in this survey.

The main criterion which has been used in this survey of suitable metals and metallic compounds is that the heat of fusion per unit mass must be large; a figure of 200 cals./gm. and a temperature of 600°C have been chosen as the lowest limits.

METALS

Only three metals are found to satisfy the suggested criteria. These are boron, beryllium and silicon.

BORON: The usually accepted melting point of boron of 2000-2075°C due to Cueilleron [1, 2] has been placed in doubt by the more recent measurements of Searcy and Myers [3] who suggest a value between 2150-2160°C. Stull and Sinke [12] give a value of 2300°K. No heat of fusion measurements have yet been made on boron but a resonable estimate can be made by assuming that the entropy of fusion is in the range of 2.1 to 2.3 e.u.[4]. This yields a heat of fusion of approximately 5300 cals./gm. mole or about 490 cals./gm. Even though the high melting point and difficult container problems militate against the use of pure boron as a possible heat sink, it is felt that boron may be a useful component in a suitable binary or more complex eutectic system.

BERYLLIUM: The melting point of beryllium is generally accepted to be 1283 $\pm$ 3°C [4, 5]. The usually accepted value for the heat of fusion of beryllium is 2800 $\pm$ 500 cal/mole [5] which gives a value of 310 $\pm$ 55 cals/gm. for the available heat.

SILICON: The recent work of Olette [8] gives the melting point for silicon as 1412 $\pm$ 2°C. Olett's figure for the heat of fusion is 12,110 $\pm$ 100 cal/gm. mole providing an available heat of 410 cals./gm.

COMPOUNDS

LITHIUM FLUORIDE: Kelley [5] gives the melting point and measured heat of fusion of lithium fluoride to be 1121.3 °K and 6.470 k. cals/gm. mol. respectively, the available heat being 250 cals/gm.

MAGNESIUM FLUORIDE: The usually accepted values of melting point and heat of fusion are 1536°K and 13.9 k. cal/gm. mole [6] respectively. This gives an available heat of 223 cals/gm.

BERYLLIUM OXIDE: Kubaschewski and Evans [4] estimate the heat of fusion to be 17 k. cals/gm. mol. Kandyba et al [9] made heat content measurements on solid and liquid BeO. From one heat content measurement on liquid BeO at 2840°K the heat of fusion was calculated to be 15.44 k.cals/gm mole [9] with an uncertainity of $\pm$ 0.5 k.cal/gm. mol. The heat of fusion had been estimated to be 14 k.cals/gm mole in the JANAF compilation [6]. Recent reported values for melting point of BeO have ranged from 2723°K to 2843°K [9a, 6]. A melting point of 2820 ± 15°K [9] was selected for this work. The available heat from different data would be 680 [4], 618 [9] and 560 [6] cals/gm. respectively.

MAGNESIUM OXIDE: The melting point as given by Kanolt [22] is 3075°K. This value is generally accepted. The heat of fusion of MgO was calculated by Kelley [23] to be 18.5k. cal./gm. mole from the depression of the freezing point in the MgO - ZrO_2 system. As this method assumes an ideal mixing of the liquid solution this value is only an approximate one and an uncertainity of 1.5 k.cal./gm mole is assigned to it. The available heat would be 464 cals/gm.

CALCIUM OXIDE: Kubaschewski and Evans [4] give the melting point of CaO as 2873°K. Schumacher [24] reported it to be 2849°K, and Kanolt [22] gave a value of 2843°K. The average for these values of 2860 ± 30°K was adopted here. Kubaschewski and Evans [4] estimated the heat of fusion to be 19.0k.cal/gm mol. Kelley [23] calculated a value of 12.24k. cal./gm. mol. from melting points in the CaO - ZrO_2 system. The available heat from the different data would be 340 [4] and 220 cals/gm. [23] respectively. Although it is almost inconceivable that the oxides themselves could be used in view of their high melting points, the eutectic mixtures in the systems CaO - BeO and MgO - BeO are practicable.

COBALT TRISILICIDE: The melting point and heat of fusion are found to be 1579°K and 34.0 ± 2.5 k.cal/gm. mole [25] respectively. The available heat would be 238 ± 15 cals/gm.

MAGNESIUM SILICIDE (Mg_2Si) The melting point and estimated heat of fusion are 1375°K [4] and 20.5 ± 2.5 k.cal/gm. mol. [4] respectively. This gives an available heat of 270 ± 30 cals./gm.

ESTIMATION OF THE HEATS OF FUSION OF EUTECTIC MIXTURES

Direct measurements of heats of fusion of most of the eutectic systems are yet to be made. It is possible however, to calculate the heats of fusion of these eutectic mixtures provided the following data are available.

(a) Integral heat of formation of liquid eutectic mixture

(b) Heat capacities of solid and liquid components

(c) Heats of formation and fusion of any intermetallic compounds taking part in eutectic reaction.

(d) Integral heat of formation of primary solid solutions, if any.

Let

X = Mole fraction of component B

$(\Delta H_f)_A$ = Heat of fusion of component A at T_A °K.

$(\Delta H_f)_B$ = Heat of fusion of component B at T_B °K.

C_{PAl} and C_{PAS} are the heat capacities of liquid and solid "A" respectively.

C_{PBl} and C_{PBS} are the heat capacities of liquid and solid "B" respectively.

ΔH^M = Integral heat of formation of liquid eutectic solution at some temperature T_M.

ΔH_{α}^M = Integral heat of formation of solid solution α at T_e.

ΔH_{β}^M = Integral heat of formation of solid solution β at T_e.

ΔC_P^M = Integral heat capacity change on mixing

$= C_P^M - (1-X_2)\, C_{PA1} - X_2\, C_{PB1}$

A mixture of pure solid elements "A" and "B" in the eutectic proportion held at the eutectic temperature T_e is taken as the reference state.

The formation of liquid eutectic at T_M from the pure liquid components can be represented by the reaction

$$X_2\, B(1) + (1 - X_2)\, A\,(1) = A_{1-X_2}\, B_{X_2}\ (1)$$

Integral heat of formation at $T_M = \Delta H^M$

From Kirchoff's law, [28] the integral heat of formation at T_e is given by

$$= \Delta H^M - \int_{T_e}^{T_M} \Delta C_P^M \, dT$$

From Kirchoff's law, the heat of fusion of component "A" at T_e

$$= (\Delta H_f)_A - \int_{T_e}^{T_A} \Delta C_P\, dT$$

$$= (\Delta H_f)_A - \int_{T_e}^{T_A} (C_{PAl} - C_{PAS})\, dT$$

The heat absorbed in melting $(1 - X_2)$ moles of "A" =

$$(1 - X_2) \left[(\Delta H_f)_A - \int_{T_e}^{T_A} (C_{PAl} - C_{PAS})\, dT \right]$$

The heat of fusion of "B" at $T_e = (\Delta H_f)_B - \int_{T_e}^{T_B} \Delta C_p dT$

$$= (\Delta H_f)_B - \int_{T_e}^{T_B} (C_{PBl} - C_{PBS})\, dT$$

Therefore, the heat absorbed in melting X_2 moles of "B" =

$$X_2 \left[(\Delta H_f)_B - \int_{T_e}^{T_B} (C_{PBl} - C_{PBS})\, dT \right]$$

Therefore for a system showing no solid solubility or if the solid solubility is neglected we have for the heat of fusion of the eutectic mixture the following expression

$$H_{(\text{liquid}-\text{eutectic})} - H_{(\text{solids})} = \left[\Delta H^M - \int_{T_e}^{T_M} \Delta C_P^M \, dT + (1-X_2)\left[(\Delta H_f)_A - \int_{T_e}^{T_A} (C_{PAl} - C_{PAS})\, dT \right] + X_2 \left[(\Delta H_f)_B - \int_{T_e}^{T_B} (C_{PBl} - C_{PBS})\, dT \right] \right]$$

The above expression gives $H_{(\text{liquid}-\text{eutectic})} - H_{(\text{pure solids})}$ and must be corrected to take into account any solid solubility.

The formation of primary solid solution "α" may be represented by the equation

$$X_1 B(S) + (1 - X_1) A(S) = A_{1-X_1} B_{X_1} (S)$$

The fraction of "α" in the eutectic mixture at "T_e" $= \dfrac{X_3 - X_2}{X_3 - X_1}$

$$\text{Heat of formation at } T_e = \Delta H_{\alpha}^M \left(\frac{X_3 - X_2}{X_3 - X_1}\right)$$

The formation of the second primary solid solution "β" is represented by

$$X_3 B(S) + (1 - X_3) A(S) = A_{1-X_3} B_{X_3} (S)$$

The fraction of "β" in solid eutectic mixture at "T_e" $= \dfrac{X_2 - X_1}{X_3 - X_1}$

Heat of formation $= \Delta H_\beta^M \left(\dfrac{X_2 - X_1}{X_3 - X_1}\right)$

$H_{(\text{solid eutectic})} - H_{(\text{solid mixture})} =$ Heat of formation of solid eutectic from pure "A" and pure "B".

$$H_{(\text{solid eutectic})} - H_{(\text{solid mixture})} = \Delta H_\alpha^M \left(\frac{X_3 - X_2}{X_3 - X_1}\right) + \Delta H_\beta^M \left(\frac{X_2 - X_1}{X_3 - X_1}\right)$$

Heat of fusion of eutectic at $T_e = \Delta H_m$

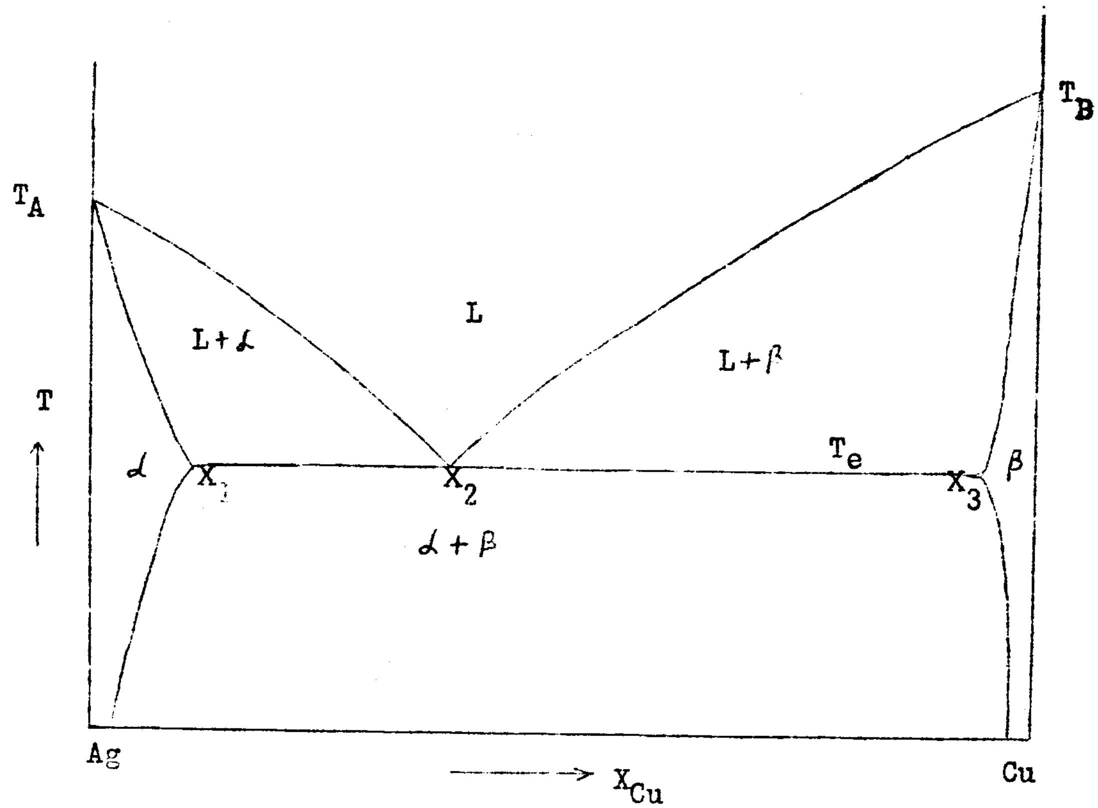
$$\Delta H_m = \left[\begin{aligned} &\Delta H^M - \int_{T_e}^{T_M} \Delta C_p^M \, dT - \Delta H_\alpha^M \left(\frac{X_3 - X_2}{X_3 - X_1}\right) - \Delta H_\beta^M \left(\frac{X_2 - X_1}{X_3 - X_1}\right) \\ &+ (1 - X_2) \left[(\Delta H_f)_A - \int_{T_e}^{T_A} (C_{PAl} - C_{PAS}) \, dT \right] \\ &+ X_2 \left[(\Delta H_f)_B - \int_{T_e}^{T_B} (C_{PBl} - C_{PBS}) \, dT \right] \end{aligned} \right]$$

TABLE I - THERMOCHEMICAL PROPERTIES OF METALS

Ref.	Metal	M.P. ^{o}K	At melting point		C_{ps}			C_{pl}	$H^{o}_{m.p.(S)} - H^{o}_{298}$
			ΔH_f cals/mol.	cals/gm.	a	$b.10^3$	$c.10^{-5}$		cals/mol.
3, 12	B	2440	5300	490	4.13	1.66	-1.76	7.50	12080
12	Be	1556	2800	310	4.58	2.12	-1.14	7.50	7920
5,8	Si	1685	12110	431	5.70	0.70	-1.04	6.10	8580
5	Co	1768	4100	69.6	17.49	-4.92	-	9.00	13040
5	Mg	923	2140	88.1	4.97	3.04	0.04	7.80	4275
7	Ag	1234	2855	26.5	5.091	2.04	0.36	7.30	6315
5	Cu	1356	3120	49.1	5.41	1.50	-	7.50	7040

$$C_p = a + bT + cT^{-2} \quad \text{cals/}^{o}\text{K - mol.}$$

This is the amount of heat obtained upon equilibrium solidification of the liquid eutectic at temperature T_e. To illustrate the procedure, an estimation was carried out on the Ag - Cu system.



Eutectic composition = 0.399 = X cu

Eutectic temperature = 1052 $^{\circ}$K

$0.399\ Cu\ (l) + 0.601\ Ag\ (l) = Cu_{0.399}\ Ag_{0.601}\ (l)$

ΔH^M at 1400 $^{\circ}$K [7] = 990 cals/gm. atom

$$\Delta H^M \text{ at } T_e = 990 - \int_{1052}^{1400} \Delta C_p^M \, dT$$

Where ΔC_p^M refers to the heat capacity change on mixing

If we apply Kopp's law [26], $\Delta C_p^M = 0$ and the temperature variation of ΔH^M is neglibible.

$$\Delta H^M \text{ at } T_e = 990 \text{ cals/gm. atom}$$

For the fusion of copper

$$0.399 \text{ cu (S)} = 0.399 \text{ cu (l)}$$

$$(\Delta H_f)_{cu} \text{ at } 1356^{\circ}K^{(5)} = 3120 \text{ cals/gm. atom}$$

$$(\Delta H_f)_{cu} \text{ at } 1052^{\circ}K = 3120 - \int_{1052}^{1356} \Delta C_p dT$$

$$= 3120 - \int_{1052}^{1356} (2.09 - 1.5 \times 10^{-3} T) \, dT$$

$= 3034$ cals/gm. atom or 1211 cals for 0.399 moles of copper

For the fusion of silver

$$0.601 \text{ Ag (S)} = 0.601 \text{ Ag (l)}$$

$$(\Delta H_f)_{Ag} \text{ at } 1234^{\circ}K^{(5)} = 2855 \text{ cals/gm. atom}$$

$$(\Delta H_f)_{Ag} \text{ at } 1052^{\circ}K = 2855 - \int_{1052}^{1235} (2.21 - 2.04 \times 10^{-3}T - \frac{.36 \times 10^{5}}{T^{2}})dT$$

= 2882 cals/gm. atom or 1732 cal. for 0.601 moles of silver

$H_{(\text{liquid eutectic})} - H_{(\text{solid mixture})} = 990 + 1211 + 1732$

= 3933 cals/gm. mole

When the liquid eutectic solidifies at 1052° K, the constituents are α and β in the following proportion.

$$\text{Fraction of } \alpha = \frac{0.951 - 0.399}{0.81} = 0.6779$$

Fraction of β = 1 - 0.6779 = 0.3221

Formation of "α"

$0.141\ cu\ (S) + 0.859\ Ag\ (S) = Cu_{0.141}\ Ag_{0.859}\ (S)$

ΔH^{M}_{α} at $1400^{\circ}K$ (7) = 730 cals/gm. mol.

Heat of formation of 0.6779 mol. of "α"

= 730 x 0.6779 = 495 cals.

Formation of "β"

$0.951\ Cu\ (S) + 0.049\ Ag\ (S) = Cu_{0.951}\ Ag_{0.049}\ (S)$

ΔH^{M}_{β} at $1400^{\circ}K$ (7) = 420 cals.

TABLE II - BINARY METALLIC SYSTEMS

Ref.	System	Eutectic Composition (X_2)	Eutectic Temp. T_e °K	X, Mole Fraction of "B" α	β	γ	ΔH^M cals/gm.atom Eutectic	α	β	Heat of fusion ΔH_m cal/mol.	cals/gm.
7,5,12	Ag-Cu	0.399	1052	0.141	0.951	-	990	730	420	3303	37
5,7	Cd-Tl	0.728	476.5			-	440	-	-	1520	8.5
5,7	Ga-Zn	0.050	298.5		-	-	75		-	1410	27
7,12	Mg-Pb	0.191	740	0.0775	Mg_2Pb 0.3333	0.941	-1820	-900	Mg_2Pb - -4200	2457	41
12,7	Mg-Pb	0.343	524	0.0775	0.3333	0.941	-520		-4200	1555	8.6
10,8,29	Co-Si	0.775	1532		$CoSi_2$ 0.6667		-6450		$CoSi_2$ -8200	9488	265
5,4	Mg-Si	0.545	1223	-	Mg_2Si 0.333			-	-	8591	326

X = Mole Fraction of "B" Component (Cu, Tl, Zn, Pb, and Si)

Heat of formation of 0.3221 mol. of " B "

$$= 0.3221 \times 420 = 135 \text{ cal.}$$

$$H_{(\text{solid eutectic})} - H_{(\text{solid mixture})} = 495 + 135 = 630 \text{ cal/gm. mol.}$$

ΔH_m = Heat of fusion of eutectic

$$= 3933 - 630 = 3303 \text{ cals/mol.}$$

Formula weight of the eutectic = 90.2 gm.

$$\text{Available heat} = \frac{3303}{90.2} = \underline{37} \text{ cals/gm}$$

The following are the most promising systems:[27]

BINARY METALLIC SYSTEMS

System	Eutectic at % Composition	Eutectic Temperature
Si - Ce	81.5% Si (Ce Si_2 - Si)	1240°C
Si - Y	82% Si (Y_3 Si_5 - Si)	1215°C
Be - Co	90% Be ($Be_{21}Co_5$ - Be)	1245°C
Be - Fe	95% B3 (Be_5Fe - Be)	1225°C
Be - Ni	90% Be (Be_{21} Ni_5 - Be)	1240°C
B - Y	98 - 98.5% B	1960 - 1970°C
B - Mo	80% B	1650 - 1680 °C
Be - Cu	82.7% Be (Be_3Cu - Be)	1150°C
Ca - Si	69% Si ($CaSi_2$ - Si)	980°C
Co - Si	77.5% Si (Co Si_2- Si)	1259°C
Mg - Si	53.5% Si (Mg_2 Si - Si)	920°C

Unfortunately most of the data are not avilable for the systems of interest. However, this method enables fragmentary data to be used and reasonable estimates of heats of fusion to be made.

OXIDES: $CaO - BeO$ and $MgO - BeO$ are the important systems. The heats of formation of these liquid eutectics are not available and the estimates are made assuming them to be zero. Batutis[21] measured the heat of fusion of 60 BeO - 40 MgO using an adiabatic calorimeter and obtained 500 cal./gm. which agrees fairly well with this estimation. Glasscock, Jr.[17] measured the heat of fusion of 60 BeO - 40 CaO by transient method and the value is 200 ± 25 cal/gm. which is in close agreement with that of Batutis[21] who gives it as 221 cal/gm. Since CaO and MgO are chemically similar it is expected that the heat of mixing and heats of fusion would not be much different. Therefore it is surprising to find this large difference between the systems BeO - MgO and BeO - CaO. Confirmation of these values would be desirable.

FLUORIDES: $LiF - NaF$, $Lif - Mg F_2$ and $CaF_2 - MgF_2$ systems are of importance and the estimated values of ΔH_m are shown.

CHLORIDES: The estimated value of heat of fusion of the eutectic $LiCl - KCl$ is 3.9 k. cal./gm. mole and the calorimetric measurements of Solomons et al[18] give a value of 3.2 k. cal./gm. mole which is in reasonable agreement with the estimate.

EFFECT OF NON-EQUILIBRIUM STRUCTURE

So far only the equilibrium eutectic structure has been considered. To obtain the equilibrium structure which is a complete separation of the two phases, the cooling rate has to be exceedingly low. For real cooling rates the typical eutectic structure is observed. This usually is a lamellar structure with large interfacial areas. Little is known about the heats associated with this. However we can draw some conclusions from the work of Mehl, Pound and Kramer [20] on lamellar pearlite. The interfacial enthalpy of the pearlite phase in $Fe - Fe_3C$ system was found to be 1400 ± 300 ergs/cm^2. For an interlamellar spacing of 6A^o in the $Fe - Fe_3C$ eutectoid structure the interfacial area would be 5800 cm^2/gm. and the total heat locked up as interfacial energy would be no more than 0.2 cal/gm. This is negligible compared to the experimental error and so the effect of non-equilibrium structure on the heat of solidification is likely to be insignificant.

CONCLUDING REMARKS

This survey yields a few systems which are of interest from the point of view of energy storage. Thermodynamic data on these interesting systems is very much lacking. Measurements of heats of fusion, heats of mixing and partial molar properties are yet to be done on almost all of these systems. For the study of transient properties precise thermochemical data is a prerequisite. Nothing has been said about the difficulties to be encountered in finding suitable containers for these systems.

TABLE III - THERMOCHEMICAL PROPERTIES OF COMPOUNDS

Ref.	Compound	M. P. ^oK	ΔH_f k. cal./mol	cals./gm.	C_{ps} (cals/^oK - mol.) a	b. 10^3	c. 10^{-5}	C_{pl}
9,13	Be O	2820	17.00	680	8.45	4.00	-3.17	16.00
24,6	Ca O	2860	19.00	340	11.86	1.08	-1.66	16.50
4,6,22	Mg O	3075	18.50	460	10.18	1.74	-1.48	14.60
6,	Li H	959.6	7.0	880	14.00	-	-	14.00
14,6	Li F	1121	6.474	250	10.41	3.90	-1.38	15.34
5,4	MgF_2	1536	13.90	224	16.90	2.52	-2.20	22.60
5,6	Na F	1285	8.030	192	10.40	3.88	-0.33	16.40
5,4	Na Cl	1073	6.9	117	10.98	3.90	-	16.00
5,4	Li Cl	883	3.20	112	11.00	3.40	-	15.50
4,5	KF	1130	6.75	116	11.02	3.12	-	16.00
6,4	CaF_2	1691	7.10	91	25.81	2.50	-	23.90
5,4	K Cl	1043	6.28	84.3	9.89	5.20	0.77	16.00

continued

TABLE III - THERMOCHEMICAL PROPERTIES OF COMPOUNDS

Ref.	Compound	M. P. ^{o}K	k. cal/ mol.	cals./gm.	C_{ps} (cals/^{o}K - mol.) a	b.10^3	c. 10^{-5}	C_{pl}
6,5,4	Li Br	823	4.22	49.0	11.50	3.02	-	16.00
5,4	SiO_2	1986	3.60	60.0	14.41	1.94	-	21.66

BINARY SYSTEMS - COMPOUNDS

Ref.	System	Eutectic Composition (X_2)	Eutectic Temp. T_e °K	ΔH^M cals/mole.	Estimated heat of fusion cals/ gm. mol.	Estimated heat of fusion cals/gm.
11,9	CaO - BeO	0.67 Be O	1738	*	20170	571.0
11,6	MgO - BeO	0.67 Be O	2143	*	19100	637.0
11,6	CaO - MgO	0.33 MgO	2573	*	19435	381.0
5,11	LiF - NaF	0.39 NaF	925	*	6734	212.0
6,5	LiF - MgF_2	0.33 MgF_2	1015	*	8440	220.0
11,6	CaF_2 - MgF_2	0.55 MgF_2	1210	*	11601	168.0
19,5	KF - LiF	0.50 LiF	765	-1210	6600	157.0
11,5	CaF_2 - NaF	0.65 NaF	1087	*	9925	182.0
6,5	LiF - LiCl	0.695 Li Cl	757	*	3889	104.0
5,11	KF - NaF	0.40 NaF	983	*	6917	134.0
18,5	Li Cl - K Cl	0.42 K Cl	623	*	3909	70.0
16,4	KNO_3-$NaNo_3$	0.50 $NaNo_3$	495	-110.6	5070	55.0

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